

PATENT SPECIFICATION

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(19)



(54) CROSS-LINKING PROCESS

(71) We, DOW CORNING LIMITED, a British Company of 12 Whitehall, London SW1A 2DZ, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a method for cross-linking ethylene-vinyl acetate copolymers and is concerned with an improvement in or modification of the invention claimed in Patent No. 1,286,460.

In Patent No. 1,286,460 there is described and claimed a process for effecting the cross-linking of a polyolefin which comprises (A) reacting a polyolefin which is polyethylene or a copolymer of ethylene with a minor proportion of propylene and/or butylene, with a silane of the general formula $RR'SiY_2$ (wherein R represents a monovalent olefinically unsaturated hydrocarbon or hydrocarbonoxy radical, each Y represents a hydrolysable organic radical and R' represents an R radical a methyl radical or a Y radical) in the presence of a compound capable of generating free radical sites in the polyolefin, the said reaction being carried out at a temperature above 140°C and the said free radical generating compound having a half-life at the reaction temperature of less than 6 minutes; and (B) subsequently exposing the product of (A) to moisture in the presence of a silanol condensation catalyst.

We have now discovered that the process described and claimed in said Patent is also applicable to the preparation of cross-linked copolymers of ethylene and vinyl acetate.

Accordingly this invention provides a process for the production of a cross-linked copolymer of ethylene and vinyl acetate which comprises (A) reacting a copolymer of ethylene and vinyl acetate with a silane of the general formula $RR'SiY_2$, wherein R represents a monovalent olefinically unsaturated radical attached to silicon through a silicon

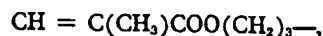
to carbon bond and composed of carbon, hydrogen and, optionally, oxygen, each Y represents a hydrolyzable organic radical and R' represents a monovalent hydrocarbon radical free of aliphatic unsaturation or a Y radical, in the presence of a free radical generating compound, the said reaction being carried out at a temperature above 140°C and said free radical-generating compound having a half-life at the reaction temperature of less than 6 minutes and (B) subsequently exposing the product of (A) to water in the presence of a silanol condensation catalyst.

The invention also includes cross-linked poly(ethylene-vinyl acetate) whenever produced by said process.

The process of this invention may be employed to effect the cross-linking of a wide range of ethylene-vinyl acetate copolymers, the preferred copolymers being those having up to 50 mole per cent, most preferably 15 to 40 mole per cent, of units derived from vinyl acetate.

If desired there may also be included with the ethylene-vinyl acetate copolymer a proportion of polyethylene free of vinyl acetate units. The proportion of the latter employed may vary widely depending on the diluent effect required but will normally not exceed that of the copolymer.

In the general formula of the silanes employed in the process of this invention, R represents a monovalent olefinically-unsaturated radical composed of carbon, hydrogen and, optionally, oxygen. Examples of such radicals are vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, cyclohexadienyl,



and



the vinyl radical being preferred. The group Y may represent any hydrolysable organic radical, for example an alkoxy radical, such as the methoxy, ethoxy and butoxy radicals, an acyloxy radical, for example the formyloxy, acetoxo or propionoxo radicals, an oximo radical e.g. $\text{—ON}=\text{C}(\text{CH}_3)_2$, $\text{—ON}=\text{CH}_2\text{C}_2\text{H}_5$, and $\text{—ON}=\text{C}(\text{C}_6\text{H}_5)_2$ or a substituted amino radical e.g. alkylamino and arylamino radicals, examples of which are —NHCH_3 , NHC_2H_5 , and $\text{—NH}(\text{C}_6\text{H}_5)$. The Y substituents in any given silane molecule may be the same or different. The group R' may represent a monovalent hydrocarbon radical free of aliphatic unsaturation e.g. methyl, ethyl, propyl, tetradecyl, octadecyl, phenyl, benzyl, or tolyl. It may also represent a Y group. Preferably the silane will have the formula RSiY_3 , wherein R is vinyl, the most preferred silanes being vinyltriethoxysilane, vinyl trimethoxysilane and combinations of these. Silanes having only two hydrolysable groups e.g. vinylmethyldiethoxysilane and vinylphenyldimethoxysilane are however also operative.

The proportion of silane employed will depend in part upon the reaction conditions and in part on the degree of modification desired in the ethylene-vinyl acetate copolymer. The actual proportion may vary widely, for example from 0.1 to 20 per cent by weight based on the weight of copolymer or of both copolymer and polyethylene when the latter is present. In general, however, we prefer to employ from 0.5 to 5 percent by weight based on the weight of the copolymer.

As the free radical generating compound there may be employed any compound which is capable of producing radical sites in the ethylene-vinyl acetate copolymer under the reaction conditions and which has a half life at the reaction temperature of less than 6 minutes, and preferably less than 1 minute. The best known and preferred free radical generating compounds for use in this invention are the organic peroxides and peresters, for example benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-tertiary butylperoxide, 2,5 - dimethyl - 2,5 - di(peroxybenzoate)hexylene - 3; 1,3 - bis(t - butylperoxyisopropyl)benzene, lauroyl peroxide, tertiary butyl peracetate, 2,5 - dimethyl - 2,5 - (t-butylperoxy)hexylene - 3; 2,5 dimethyl - 2,5 - di(t - butylperoxy)hexane and tertiarybutyl perbenzoate, and azo compounds, for example azobis-isobutyronitrile and dimethylazodi-isobutyrate; dicumyl peroxide being the most preferred.

The particular free radical generating compound chosen in any instance will depend upon the temperature at which reaction of the ethylene-vinyl acetate copolymer with the silane

is to be performed. Thus if the reaction is to be performed at, say, from 160 to 180°C benzoyl peroxide or dicumyl peroxide, which have appropriate half-lives at these temperatures, can be used.

Sufficient of the free radical generator should be used to obtain the desired degree of modification of the copolymer. However, the proportion should not be so high as to cause degradation of the copolymer or free-radical cross-linking of the copolymer to become the predominant mechanism. The proportion required will depend to some extent on the nature of the free radical generator itself. Some peroxide compounds may be employed in relatively high proportions, e.g. up to 1.5% by weight based on the weight of the copolymer, without causing significant convention peroxide cross-linking to occur. However, when the free radical generating compound is effective in producing conventional free radical cross-linking we prefer to employ not more than about 0.75 per cent by weight of the free radical generating compound based on the weight of the copolymer. As little as 0.005 per cent of the free radical generator may be used and will give rise to some cross-linking capability in the ethylene-vinyl acetate copolymer in the process of this invention. For most applications, however, we prefer to use from 0.01 to 0.2 per cent by weight based on the weight of the copolymer.

In accordance with Step (A) of the process of this invention reaction between the ethylene-vinyl acetate copolymer and the silane is carried out at a temperature above 140°C. The reaction may be carried forward employing any suitable apparatus. Preferably however, the reaction is carried forward under conditions in which the copolymer is subjected to mechanical working. The reaction is therefore preferably carried out in, for example, an extruder, an internal Banbury mixer or a roll mill provided it permits the copolymer to reach the desired temperature. The most preferred form of apparatus is that of the type which comprises a closed extruder adapted to effect a kneading or compounding action on its contents. One such type of apparatus is that known as the Ko-Kneader which is adapted to accomplish mechanical working and compounding of plastics at elevated temperatures.

The ethylene-vinyl acetate copolymer and silane reactants may be brought together by any convenient means. For example the liquid silane may be introduced into the apparatus in which the reaction is to take place dispersed on the surface of the copolymer or it may be metered directly into the apparatus. The free radical generating compound may also be introduced by way of the surface of the co-

polymer or may be added, when solubility considerations permit, as a solution in the silane.

Reaction between the silane and the ethylene-vinyl acetate copolymer may be carried forward at any temperature between 140°C and the degradation temperature of the copolymer. The actual reaction temperature employed will normally be determined by consideration such as the type of apparatus in which the reaction is performed and on the power input for the apparatus. It will also depend on the temperature at which degradation of the copolymer occurs. We prefer to perform the reaction at temperatures in the range from about 140 to 220°C for periods of up to 10 minutes.

Although minor amounts of organic solvents may be employed if desired to facilitate the addition of the free radical generator or the silane the reaction is usually best carried out in bulk since this avoids subsequent tedious solvent removal procedures.

Cross-linking of the silane-modified ethylene-vinyl acetate copolymer according to Step (B) of the process of this invention is effected by exposing the product of Step (A), usually after shaping by extrusion or other processes, to water in the presence of a silanol condensation catalyst. The moisture present in the atmosphere is usually sufficient for cross-linking to occur but the rate of cross-linking may be hastened if desired by the use of an artificially moistened atmosphere or immersion in liquid water, optionally employing elevated temperatures. Preferably cross-linking is effected at a temperature between 50°C and about 80°C.

Provided the reaction product of the ethylene-vinyl acetate copolymer and the silane is kept free of moisture and/or of material which acts as a silanol condensation catalyst it may be stored if desired. As it is often difficult to exclude all traces of moisture from the copolymer the preparation of a product which remains substantially unchanged over a long storage period is usually only possible when the hydrolysable moieties in the silane are those, such as alkoxy radicals, which give rise to non-catalytic by-products. When the silane contains, for example, silicon-bonded acetoxy radicals or even trace quantities of silicon-bonded chlorine atoms the acetic acid or hydrochloric acid by-products can cause some cross-linking to occur at normal ambient temperatures if moisture has not been excluded from the composition.

If a storage stable product is not desired the use of a silane or other additive which generates a silanol condensation catalyst *in situ* during hydrolysis may be permissible, or even preferred. In general, however, we prefer to incorporate the silanol condensation catalyst into the product of Step (A) only when it is desired to initiate cross-linking of the product,

for example, just prior to shaping into the finished article. Thus, for example, Step (A), the addition of the silanol condensation catalyst and shaping of the cross-linkable product may take place continuously, for example by performing all of the operations in a single compounding extruder. Alternatively the cross-linkable copolymer composition can be provided in the form of two separate components, one component comprising the copolymer which has been modified according to Step (A) of the process of this invention, the other component comprising a composition obtained by mixing the silanol condensation catalyst with ethylene-vinyl acetate copolymer, or if desired polyethylene itself, which has not been modified by reaction with the silane. The two components may then be blended in the desired proportions to provide a composition which is cross-linkable in the presence of water. In order to obtain a copolymer having the maximum degree of cross-linking capability the unmodified ethylene-vinyl acetate copolymer preferably comprises not more than about 10 percent by weight of the total quantity of ethylene-vinyl acetate copolymer in the mixed composition. When preparing a cross-linkable copolymer by this technique therefore we prefer to employ from about 1 to 10 per cent by weight of the unmodified copolymer catalyst component based on the total copolymer content of the composition. Preferably also the polyethylene or copolymer used in the catalyst component has flow characteristics which are the same as, or approximate to that of the silane-modified copolymer with which it is to be mixed.

Any of the wide variety of materials which function as silanol condensation catalysts may be employed in the process of this invention. Such materials include, for example, metal carboxylates such as dibutyltin dilaurate, stannous acetate, stannous octoate, lead naphthenate, zinc octoate, iron-2-ethylhexoate and cobalt naphthenate, organic metal compounds such as the titanium esters and chelates, for example tetrabutyl titanate, tetranonyl titanate and bis-acetylacetonyl-di-isopropyl titanate, organic bases such as ethylamine, hexylamine, dibutylamine and piperidine and acids such as the mineral acids and fatty acids. The preferred catalysts are the organic tin compounds, for example dibutyltin dilaurate, dibutyltin diacetate, and dibutyltin dioctoate.

Having regard to the considerations discussed hereinabove the silanol condensation catalyst may be incorporated prior to, during, or following the reaction of the ethylene-vinyl acetate copolymer and the silane. The catalyst may be added as such or generated *in situ* either by hydrolysis of the silane or, for example, by the thermal decomposition of a material which liberates an amine or other silanol condensation catalyst as a decomposition product.

Another method of employing the catalyst which can be used is described in our co-pending Application No. 52548/71 (Specification No. 1,357,549) and comprises contacting the product of Step (A) with an aqueous dispersion or solution of an organic tin compound.

In addition to the presence of the silanol condensation catalyst or precursor thereof the copolymer may contain, if desired, other ingredients, for example fillers and pigments.

Cross-linked ethylene-vinyl acetate copolymer produced according to this invention possesses improved strength at elevated temperature, improved compression set resistance and improved air oven ageing properties. The process of the invention may therefore be advantageously employed in the provision of electrical insulation and articles such as containers and conduits for hot liquids. The process may also be employed in the preparation of adhesives and cross-linked film.

Cross-linked ethylene-vinyl acetate copolymer having a cellular structure can be obtained by incorporating a silanol condensation catalyst and a heat-activated blowing agent with the product of Step (A). The resulting composition may then be foamed and cross-linked by exposure to a temperature at which the blowing agent is activated and to water. Any of the heat activated blowing agents which are suitable for the foaming of olefinic polymers may be employed. Typical of such materials are azodicarbonamide, di-nitrosopentamethylene tetramine, benzene sulphonyl hydrazide, sodium bicarbonate and ammonium carbonate.

Prior to the application of Step (B) the cross-linkable ethylene-vinyl acetate copoly-

mers prepared according to Step (A) may, if desired, be blended with polyethylene itself or with polyethylene or chlorinated polyethylene which has been rendered cross-linkable by a similar process.

The following examples, in which the parts are expressed by weight, illustrate the invention.

Example 1.

The ethylene-vinyl acetate copolymer employed in this example was that available commercially at UE 643 containing approximately 20 mol per cent of vinyl acetate and having a melt flow index of 9.0 g./10 min. 100 parts of this copolymer in chip form were tumbled with a solution of 0.1, 0.2 or 0.3 parts of dicumyl peroxide in 2.0 parts of vinyl trimethoxysilane until all of the solution was dispersed over the copolymer surface. This material was then passed through a Buss PR 46 Ko-Kneader at a rate of approximately 100 g/min., both the kneading and granulating screws of the apparatus being operated at a temperature of 207°C. The polymer was recovered in the form of pellets and pressed at 180°C into sheets having a thickness of 3 mm.

Cross-linking of the copolymer sheets was brought about by immersing the sheets for 20 hours in a 5% by weight aqueous emulsion of dibutyltin dilaurate maintained at 80°C. The degree of cross-linking obtained in each case was determined by measuring the content of insoluble material in the treated sheet. This measurement was carried out by Soxhlett extraction of the material in trichloroethylene for 20 hours. The results obtained are shown in the following table, together with a comparative value for untreated copolymer.

Peroxide	Silane	Gel content %
0	0	0
0.1 pts.	2.0 pts.	77
0.2	77
0.3	73

Example 2.

The procedure of Example 1 was repeated employing three different levels of dicumyl peroxide. Melt flow indices (M.F.I.) of the

grafted copolymers, that is, prior to immersion in dibutyltin dilaurate emulsion, were measured. The melt flow indices and gel contents obtained were as follows:

Peroxide (pts)	MFI (g./10 min)	Gel Content (%)
0.10	0.41	71.3
0.05	0.72	71.0
0.04	2.59	72.3

Samples of the grafted copolymers prepared according to this Example were each compounded with 0.45% by weight of a blowing agent (Genitron EPA — Registered Trade Mark) and 5.3% by weight of a catalyst masterbatch prepared by mixing 0.25 parts of dibutyltin dilaurate with 100 parts of low density polyethylene.

The compositions were injection moulded at 220°C and the moulded products recovered as plates having a cellular structure and a thickness of 1.25 cm. When the plates were immersed in water at about 70°C for 24 hours the resulting products had a gel content of about 70%.

WHAT WE CLAIM IS:—

1. A process for the production of a cross-linked copolymer of ethylene and vinyl acetate which comprises (A) reacting a copolymer of ethylene and vinyl acetate with a silane of the general formula $RR'SiY_2$, wherein R represents a monovalent olefinically unsaturated radical attached to silicon through a silicon to carbon bond and composed of carbon, hydrogen and, optionally, oxygen, each Y represents a hydrolysable organic radical and R' represents a monovalent hydrocarbon radical free of aliphatic unsaturation or a Y radical, in the presence of a free radical generating compound, the said reaction being carried out at a temperature above 140°C and the said free radical-generating compound having a half-life at the reaction temperature of less than 6 minutes and (B) subsequently exposing the product of (A) to water in the presence of a silanol condensation catalyst.

2. A process as claimed in claim 1 wherein the ethylene-vinyl acetate copolymer contains from 15 to 40 mole per cent of units derived from vinyl acetate.

3. A process as claimed in claim 1 or claim 2 wherein the silane has the formula $RSiY_2$, and Y is as defined in claim 1.

4. A process as claimed in claim 3 wherein the silane is vinyltrimethoxysilane and/or vinyltriethoxysilane.

5. A process as claimed in any one of the preceding claims wherein the silane is employed in a proportion of from 0.5 to 5 per cent by weight based on the weight of the ethylene-vinyl acetate copolymer.

6. A process as claimed in any one of the preceding claims wherein the silanol condensation catalyst is an organic tin compound.

7. A process as claimed in any one of the preceding claims which also includes the steps of incorporating with the product of Step (A) a silanol condensation catalyst and a heat-sensitive blowing agent for the resulting composition, the composition thereafter being foamed and cross-linked by exposure to a temperature at which the blowing agent is activated and to water.

8. A process as claimed in any one of the preceding claims wherein the free radical generator is employed in a proportion of from 0.005 to 0.75 parts based on the weight of copolymer.

9. A process for the production of a cross-linked copolymer of ethylene and vinyl acetate substantially as described with reference to the Examples.

10. A cross-linked copolymer of ethylene and vinyl acetate whenever obtained by the process claimed in any one of the preceding claims.

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